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Supplemental Material for Experimental Section

2.4.8.suppl (SiMA)III The homopolymer was prepared in manner similar to P(SiMA)II (Section 2.4.4) except two aliquots of regenerated TASHF2 used as discussed in the Results and Discussion Section.

2.4.9.suppl P(*t*-BMA)I The *t*-BMA was added to a reactor at -15 °C. Several aliquots of TASHF2 (8.4% total relative to the initiator) were added to the reactor at ambient temperature but little increase in conversion occurred until the last two aliquots of TASHF2 were added. The second to last aliquot (2% relative to the initiator) raised the temperature of the reactor 16 °C in less than a min. The polymerization was quenched after GC showed 90% of the *t*-BMA was converted.

2.4.10.suppl P(*t*-BMA)II The *t*-BMA was added with a cofeed of 0.5 mol % TASHF2 (relative to MTSDA) to a reactor at -65 °C which had already been charged with MTSDA and TASHF2. The initial conversion was 20%. Several aliquots of TASHF2 (4.8% total relative to the initiator) were added to reactor at -65 °C with no observable temperature increase or further conversion of *t*-BMA over the next 4.5 h. These additions of TASHF2 in acetonitrile initially precipitated in the surface of the solution in the reactor which was at -65 °C, but were gradually dissolved. The reactor was allowed to warm to ambient temperature, and over next 60 h conversion of the *t*-BMA increased to 95%.

2.4.11.suppl P(*t*-BMA)III The *t*-BMA was added with a cofeed of 0.5 mol % TASHF2 (relative to MTSDA) to a reactor at ambient temperature which had already been charged with MTSDA and TASHF2. The conversion gradually increased to 65% after 18 h but then did not increase further over the next 26 h. The reactor was cooled to -65 °C, and additional catalyst was added (3.8% total, 2.5% additional relative to the initiator). The reactor was then allowed to warm to ambient temperature after which the *t*-BMA conversion was greater than 99%.

2.4.12.suppl P(*t*-BMA)IV The homopolymer was prepared in a manner similar to P(*t*-BMA-ran-SiMA)I (section 2.4.7) except with no SiMA and the *t*-BMA had a cofeed of

0.5 mol % TASHF2 (relative to MTSDA). Initial conversion of *t*-BMA was 40%. Several aliquots of TASHF2 (7.5% total relative to the initiator) were added to reactor at -44 °C but no increase in conversion occurred until the last aliquot of TASHF2 was added. The last aliquot (2% relative to the initiator) raised the temperature of the reactor 39 °C in less than a min and increased the conversion of *t*-BMA to greater than 99%.

2.4.13.suppl P(*t*-BMA-*b*-SiMA)IV The SiMA block was prepared in a manner similar to P(SiMA)II (Section 2.4.4). The *t*-BMA was added to a reactor at ambient temperature after which conversion gradually increased to 80% after 18 h but then did not increase further over the next 26 h. The reactor was cooled to 0 °C, and additional catalyst was added (3.0% total, 1.8% additional relative to the initiator) and the conversion of the *t*-BMA increased to 90%. An additional aliquot of catalyst was added to the reactor (4.8% total, 1.8% additional relative to the initiator) and the conversion of *t*-BMA increased to 97 %.

2.4.14.suppl P(*t*-BMA-*b*-SiMA)V The SiMA block was prepared in a manner similar to P(SiMA)II (Section 2.4.4). A portion of the *t*-BMA was added to a reactor at ambient temperature but, similar to P(*t*-BMA-*b*-SiMA)III (Section 2.4.6), additional catalyst (resulting in a total of 10% TASHF2 relative to initiator) was added to start the GTP of the *t*-BMA block before completing the addition of the *t*-BMA. The conversion of *t*-BMA gradually increased to 85% over the next 20 h. A second aliquot of catalyst (2.4% additional relative to the initiator) was added and the conversion of the *t*-BMA was increased to 87% after which the polymerization was quenched with methanol.

2.4.15.suppl P(*t*-BMA-*ran*-SiMA)II The copolymer was prepared in a manner similar to that of P(*t*-BMA-*ran*-SiMA)I (section 2.4.7).

Supplemental Material for Interpretation of ^1H -NMR Spectra of Copolymers Containing Both *tert*-Butyl Methacrylate (*t*-BMA) and 3-Methacryloxypropylpentamethyldisiloxane (SiMA) monomer units

Figure 4 shows the ^1H -NMR spectra for poly(*t*-BMA-*b*-SiMA). The chemical structure of the polymer is shown in Figure 1.supp along with peak assignments. Using the area associated with the various protons, the monomeric composition can be determined for both block and random copolymers containing *t*-BMA and SiMA.

Figure 1.supp here

SiMA has 19 protons (e, g and h) which do not overlap with those of *t*-BMA. The area associated with these 19 protons is proportional to the moles of SiMA in the copolymer as given by equation 1.supp where *k* is a proportionality constant.

$$\frac{\text{Area of e, g \& h}}{19 \text{ protons}} = \frac{\text{Area}}{\text{SiMA Proton}} = k \times \text{moles SiMA} \quad \text{Eq (1.supp)}$$

The area associated with the 14 protons of *t*-BMA is proportional to the moles of SiMA in the copolymer as given by equation 2.supp where *k* is the same proportionality constant used in equation 1.supp.

$$\frac{\text{Area}_{0.7 \text{ to } 2.5 \text{ ppm}} - 7 \times \left(\frac{\text{Area}}{\text{SiMA Proton}} \right)}{14 \text{ protons}} = k \times \text{moles } t\text{-BMA} \quad \text{Eq (2.supp)}$$

The weight ratio of SiMA in the copolymer is given by equation 3.supp using the values obtained from equations 1.supp and 2.supp.

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$$\frac{k \times \text{moles SiMA} \times \text{MW}_{\text{SiMA}}}{k \times \text{moles SiMA} \times \text{MW}_{\text{SiMA}} + k \times \text{moles } t\text{-BMA} \times \text{MW}_{t\text{-BMA}}} = \left(\frac{\text{wt } \%}{\text{SiMA}} \right)$$

Where:

$\text{MW}_{\text{SiMA}} = 274.5 \text{ g/mol}$

$\text{MW}_{t\text{-BMA}} = 142.2 \text{ g/mol}$

Eq (3.sup)

Supplemental Material for Confirmation of Structure of Polymers by NMR.

In the case of SiMA and *t*-BMA copolymers, the peak from 15.9 to 16.65 ppm is characteristic of the rr triad for the SiMA-SiMA-SiMA compositional triad. This assumes that *t*-BMA-SiMA-SiMA and *t*-BMA-SiMA-*t*-BMA compositional triads do not contribute significantly to this peak. The area under the normalized spectrum of the random copolymer from 15.9 to 16.65 ppm was calculated by summing the values. This area is proportional to N_{SiMA-SiMA-SiMA} as shown in equation 4.supp.

$$N_{\text{SiMA-SiMA-SiMA}} = k \times A(15.9 - 16.65 \text{ ppm})_{\text{Exper}} \quad \text{Eq (4.supp)}$$

where:

k is a proportionality constant

$A(15.9 - 16.65 \text{ ppm})_{\text{Exper}}$ is the area underneath the normalized experimental spectrum from 15.9 to 16.65 ppm.

We assume that the difference between the area under the homopolymer summation and the area under the experimental curve from 15.9 to 16.65 ppm is equal to the area associated with the mixed triads for SiMA as shown in equation 5.supp.

$$N_{\text{SiMA-SiMA-tBMA}} + N_{\text{tBMA-SiMA-tBMA}} = k \times A(15.9 - 16.65 \text{ ppm})_{\text{Difference}} \quad \text{Eq (5.supp)}$$

where:

$$A_{\text{Difference}} = A(15.9 - 16.65 \text{ ppm})_{\text{sum}} - A(15.9 - 16.65 \text{ ppm})_{\text{Exper}}$$

$A(15.9 - 16.65 \text{ ppm})_{\text{sum}}$ is the area underneath the summation of the properly normalized homopolymer spectra from 15.9 to 16.65 ppm.

There is no way to separate the area caused by $N_{\text{tBMA-SiMA-SiMA}}$ and $N_{\text{tBMA-SiMA-tBMA}}$. Thus, it is not possible to determine the denominator of equation 2. However, minimum and maximum boundaries can be set using equation 6.supp.

$$\left(\frac{N_{t\text{BMA-SiMA-}t\text{BMA}} +}{0.5 \times N_{\text{SiMA-SiMA-}t\text{BMA}}} \right) \geq 0.5 \times k \times A(15.9-16.65\text{ppm})_{\text{Difference}}$$

and

$$\left(\frac{N_{t\text{BMA-SiMA-}t\text{BMA}} +}{0.5 \times N_{\text{SiMA-SiMA-}t\text{BMA}}} \right) \leq k \times A(15.9-16.65\text{ppm})_{\text{Difference}}$$

Eq (6.supp)

Using equations 4.supp-6.supp, equation 2 can be converted to equation 7.supp.

$$n_{\text{SiMA}} = \frac{k \times A(15.9 - 16.65\text{ppm})_{\text{sum}}}{r \times k \times A(15.9-16.65\text{ppm})_{\text{Difference}}} \quad \text{Eq (7.supp)}$$

where:

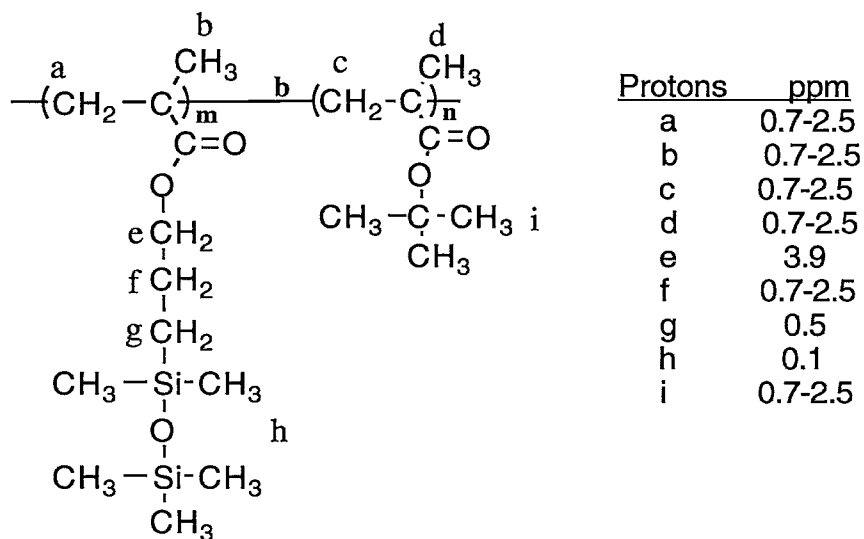
$$0.5 \leq r \leq 1.0$$

$A(15.9-16.65 \text{ ppm})_{\text{Exper}}$ and $A(15.9-16.65 \text{ ppm})_{\text{Sum}}$ were determined by summing the values between 15.9-16.65 ppm and are shown in Table 1.supp. Using the values of Table 1.supp and equation 7.supp, a range can be determined for the number average sequence length of SiMA as shown in Table 8. No characteristic peak for *t*-BMA exists, which is both affected by a neighboring SiMA monomer unit and not overlapping with the peaks due to the SiMA. Therefore, the experimental number average sequence length can not be determined for *t*-BMA.

Table 1.supp here.

The number average sequence length as calculated from equation 4.supp is most likely an over estimate. For example, the baseline of the normalized experimental spectrum from 15.9 to 16.65 ppm was not adjusted to eliminate the contribution of the large mixed triad peaks from 16.65 to 17.55 ppm. Also, the summation was shifted to overlap the experimental spectrum as much as possible. As mentioned earlier, this shifting causes

analysis of the random copolymer to overestimate the nonrandom distribution of SiMA units along the polymer chain. Even with the inflated value given by equation 2, the average number of SiMA units in a row is between 2.3 and 4.5. This compares to the block copolymer which has an area underneath the normalized experimental spectrum from 15.9 to 16.65 ppm nearly equal to the that of the homopolymer summation. Therefore, within experimental error, the block copolymer has a number average sequence length equal to the length of the SiMA block (36 SiMA units). Thus, no tapering between the blocks is apparent.

Figure 1.supp Structure and chemical shifts of protons for *t*-BMA/SiMA copolymersTable 1.supp. Values for areas of interest for P(*t*-BMA-*ran*-SiMA)II.

A(15.9-16.65 ppm)Exper	5.1
A(15.9-16.65 ppm)Sum	2.9
A(15.9-16.65 ppm)Difference	2.2